

Convenient, Efficient Crown Ether-containing Stationary Phases for Chromatographic Separation of Alkali Metal Ions: Dynamic Coating of Highly Lipophilic Crown Ethers on Octadecylsilanized Silica

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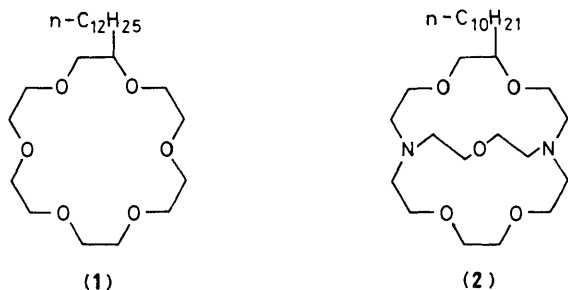
Novel immobilization of highly lipophilic crown ether derivatives by coating the crown ethers onto insoluble supports through hydrophobic interactions provides stationary phases for efficient chromatographic separation of alkali metal ions.

Immobilized crown ethers are very useful for separation, purification, and analysis of metal ions, especially those of the alkali and alkaline earth metals. In most cases, crown ether resins or chemically-immobilized crown ethers, in which crown ether moieties are chemically bonded to crosslinked polymers¹ or silica gel,² have been employed for chromatographic separation of the metal ions^{1,2} and their isotopes.³ However, these immobilized crown ethers are neither easy to synthesize nor inexpensive.

It occurred to us that hydrophobic interactions may be used for immobilizing crown ethers on insoluble supports with hydrophobic surfaces, and that this type of immobilization would be readily feasible, not being accompanied by any chemical reaction. We report here on the novel immobilization of lipophilic crown ethers on octadecylsilanized (ODS) silica and their use in chromatography of alkali metal ions.

Dodecyl-18-crown-6⁴ (**1**) and decyl-cryptand [2.2.1] (**2**) (Kryptfix 221, Merck) were chosen as the lipophilic crown ethers. Taking advantage of the high column efficiency of commercially available packed columns, we adopted a dynamic coating procedure⁵ to immobilise the crown ether derivatives, by flowing an MeOH-H₂O (200 ml) solution containing *ca.* 50 mg of the crown ether through a column (6 mm i.d., 100 mm length) packed with ODS-silica (5 μm, spherical, 20% carbon content). When 40 or 60% methanolic solutions were used for coating (**1**) and (**2**), respectively, most of the initial amounts of the crown ethers were immobilized on the ODS-silica.

Chromatography of alkali metal ions was carried out with MeOH-H₂O eluents containing not more than 50% MeOH, using a conductivity detector. For chromatography on the ODS-silica coated with (**1**), the retention time increased in the order Li⁺ < Na⁺ < Cs⁺ < Rb⁺ < K⁺, which reflects the cation-complexing properties of (**1**). Chromatography of the alkali metal ions is also affected by the counter anion, and the retention of the metal ions in the presence of different anions was enhanced in the order Cl⁻ < Br⁻ < I⁻ << SCN⁻, as is the case with chemically-immobilized crown ethers.^{1,2} The typical chromatogram of alkali metal iodides on the (**1**)-coated ODS-silica is depicted in Figure 1, which shows high separation efficiency for the stationary phase. On the other hand, the (**2**)-coated ODS-silica retained alkali metal ions in the following order, Cs⁺ *ca.* = Li⁺ *ca.* = Rb⁺ < K⁺ << Na⁺.



Since the peak for Na⁺ was broad even for elution with pure H₂O, probably because of the powerful complexing and the slow complexation equilibrium of (**2**), the (**2**)-coated ODS-silica is rather impractical as the stationary phase for h.p.l.c. It may, however, be useful for column chromatography.³

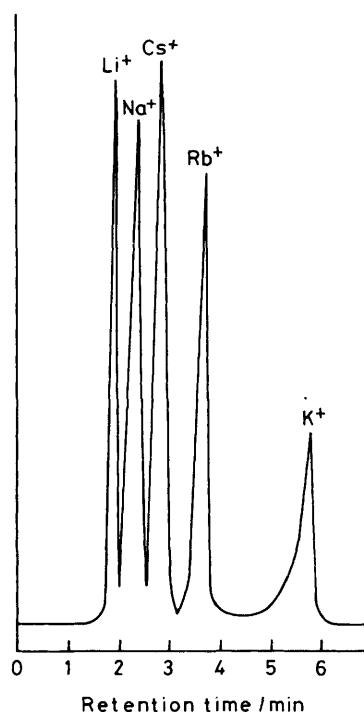


Figure 1. Chromatographic separation of alkali metal iodides on (**1**)-coated ODS-silica [eluent MeOH-H₂O (50:50); flow rate 1 ml/min; sample size 50 μl of 4 × 10⁻² mol/l salt].

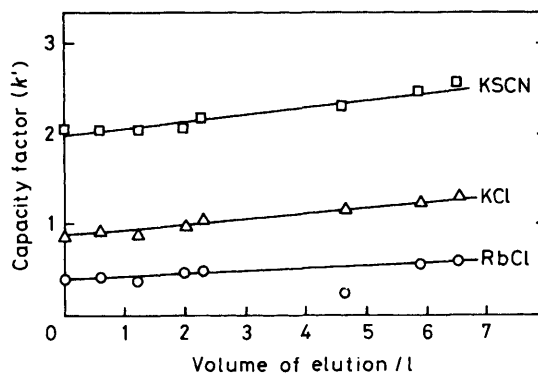


Figure 2. Stability check of (**1**)-coated ODS-silica [eluent MeOH-H₂O (40:60); flow rate 1 ml/min].

The main problem in this type of stationary phase is that the lipophilic crown ethers still tend to dissolve out from the ODS-silica during chromatography, especially with eluents of high MeOH content. Normally, the retention of metal ions on crown ether-containing stationary phases is promoted with increasing MeOH content of the eluents. Therefore, the concentration of the MeOH-H₂O eluents may be crucial in some cases. The stability of (1)-coated ODS-silica was tested using an MeOH-H₂O (40:60) eluent, which allows excellent separation of alkali metal ions in the stationary phase. It is of note that no decrease was observed in the capacity factor even after elution with 7l of the solvent, which took more than 100 h with a flow rate of 1 ml/min (Figure 2). This finding indicates that the immobilisation of (1) on the ODS-silica is stable. The high lipophilicity of the crown ether derivatives compared to the crown ethers might enhance the immobilization on the support.

Thus, this type of immobilized crown ether is easy to make and is promising as a stationary phase for ion chromatography, and may also find application in isotope separation. Another advantage is that regeneration of the stationary phases and

exchange from one crown ether to another can be made without difficulty.

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References

- 1 E. Blasius, K.-P. Janzen, W. Adrian, G. Klautke, R. Lorscheider, P.-G. Maurer, V. B. Nguyen, T. Nguyen Tien, G. Scholten, and J. Stockemer, *Fresenius' Z. Anal. Chem.*, 1977, **284**, 337; E. Blasius and K.-P. Janzen, in 'Topics in Current Chemistry,' ed. F. L. Boschke, Springer-Verlag, Heidelberg, 1981, vol. 98, p. 163; P. Kutchukov, A. Ricard, and C. Quivoron, *Eur. Polym. J.*, 1980, **16**, 753; Y. Frere and P. Gramain, *Makromol. Chem.*, 1982, **183**, 2163.
 - 2 K. Kimura and T. Shono, *J. Liq. Chromatogr.*, 1982, **5** (suppl. 2), 223; M. Nakajima, K. Kimura, and T. Shono, *Anal. Chem.*, 1983, **55**, 463.
 - 3 K. G. Heumann and H.-P. Schiefer, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 406; S. Fujine, K. Saito, and K. Shiba, *J. Nucl. Sci. Technol.*, 1983, **20**, 439.
 - 4 I. Ikeda, S. Yamamura, Y. Nakatsuji, and M. Okahara, *J. Org. Chem.*, 1980, **45**, 5355.
 - 5 R. M. Cassidy and S. Elchuk, *Anal. Chem.*, 1982, **54**, 1558.
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